

METAL-SILICATE PARTITIONING OF Bi, In, AND Cd AS A FUNCTION OF TEMPERATURE AND MELT COMPOSITION. N. Marin¹, K. Righter², L. Danielson², K. Pando², C. Lee³, ¹School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85287 (Nicole.marin@asu.edu), ²Johnson Space Center, Houston, TX 77058, ³Department of Earth Science, Rice University, Houston, TX 77005

Introduction: The origin of volatile elements in the Earth, Moon and Mars is not known; however, several theories have been proposed based on volatile elements such as In, As, Se, Te and Zn which are in lower concentration in the Earth, Moon, and Mars than in chondrites. Explanations for these low concentrations are based on two contrasting theories for the origin of Earth: equilibrium core formation versus late accretion. One idea is that the volatiles were added during growth of the planets and Moon, and some mobilized into the metallic core while others stayed in the mantle (e.g., [1]). The competing idea is that they were added to the mantles after core formation had completed (e.g., [2]). Testing these ideas involves quantitative modeling which can only be performed after data is obtained on the systematic metal-silicate partitioning behavior of volatile elements with temperature, pressure and melt composition. Until now, such data for Bi, In, and Cd has been lacking. After conducting a series of high pressure, high temperature experiments, the metal-silicate partition coefficients of Bi, In, and Cd as a function of temperature and melt composition can be used to evaluate potential conditions under which terrestrial planets differentiated into core and mantle, and how they acquired volatiles.

Procedure: Experiments were conducted at constant pressure and variable temperatures using a non-end-loaded piston cylinder apparatus with a Type C W-Re thermocouple at NASA-JSC. The sample was prepared for these experiments by grinding and mechanically mixing a powder composed of 70 wt. % Knippa basalt (the composition of which is described in [3]), 24 wt. % Fe, and 2 wt. % each Bi₂O₃, In₂O₃, SnO₂ (90:10 wt %), and Cd. Polycrystalline MgO, and graphite were the two capsule types used in an assembly with a BaCO₃ pressure medium. Upon reaching a constant pressure of 1.0 GPa, samples were heated to silicate superliquidus temperatures for durations based on equilibration times from previous experiments ([4], [5]). Afterwards, the samples were power quenched to glass or polyphase quench crystals surrounding large metallic liquid spheres. Three different experiment series were performed including a time series with graphite capsules, and two temperature series from 1500 to 1900°C, each using different capsules (either MgO or graphite) for a total of 14 experiments.

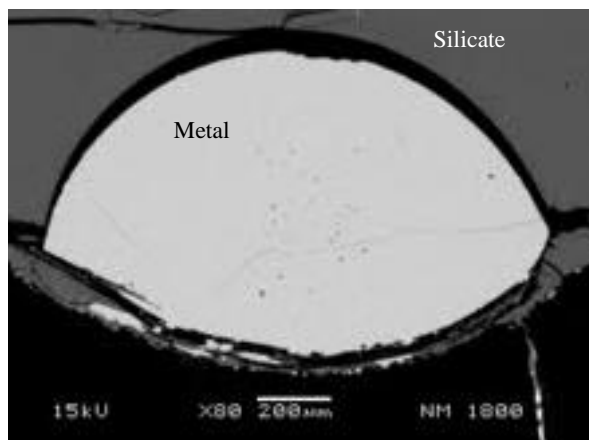


Fig. 1. Back scattered electron (BSE) image of sample NM- 1800 run at 1800°C for 15 min. The sample resulted in quenched metallic liquid (lightgray) surrounded by silicate glass (dark gray) which is encased in the graphite capsule (black).

Analysis: Figure 1 is a back scattered electron (BSE) image from the scanning electron microscope (SEM) of sample NM1800. The bright phase is a metal sphere that equilibrated with the silicate melt (the darker phase). For experiments carried out with graphite capsules, all metals were carbon saturated. The metal and silicate regions were analyzed for major element composition using a Cameca SX100 for electron microprobe analysis (EMPA) at NASA-JSC. A 1 μ m beam was used at 20kV and 10nA. Also, a variety of natural and synthetic standards were used. In each sample, the Bi, In, and Cd content of the glass was lower than the detection limit of the EMPA; therefore, the samples were analyzed for trace element composition using Laser Ablation Inductively Coupled Mass Spectrometer (LA-ICP-MS) at Rice University [1]. Standards used for the laser analysis were NIST610, NIST612, BHVO2g, and BCR2g glasses. Analysis was performed at Low Resolution (LR) and normalized to ⁴³Ca isotope. The only trace elements specifically studied for this research were ⁴²Ca, ⁴³Ca, ¹¹¹Cd, ¹¹⁰Cd, ¹¹⁵In, ¹¹⁷Sn, ¹¹⁸Sn, ¹¹⁹Sn, ²⁰⁹Bi, ⁶⁹Ga, and ⁷¹Ga. Data from the analysis of ²⁰⁹Bi, ¹¹¹Cd, and ¹¹⁵In at LR was used to calculate Cd, In and Bi in ppm in the silicates.

Results and Discussion: MgO capsules introduced increased MgO in the melt toward peridotitic composition (Figure 2) as temperature increased, and thus have application to peridotite magma ocean scenarios.

Anthracophobic behavior is exhibited by In, as indicated by the upper limit $D_{In}[\text{Metal/Silicate}]$ values for the graphite capsule experiments (Figure 3). These values are below the detection threshold of the electron microprobe. The partitioning behavior of In in graphite capsules with added sulfur is shown in data from Kelly Nickodem 2011. Sulfur effectively increases the $D_{In}[\text{Metal/Silicate}]$ values for the graphite capsules toward those of the MgO capsule experiments.

Similar behavior is seen in the Cd series, as the $D_{Cd}[\text{Metal/Silicate}]$ values are also upper limit. Additionally, a dramatic drop in $D_{Cd}[\text{Metal/Silicate}]$ occurred in the MgO series (Figure 4).

Conclusions: Overall, these experimental trends show that the equilibrium model for core formation is possible if the conditions under which the core formed were around 2000 to 3000 °C. Further experiments would need to be conducted at higher temperatures to adequately test this hypothesis. Solid metal-liquid metal Fe-FeS experimental data would also be valuable in determining the effect of sulfur on the partitioning behavior of these Bi, In and Cd.

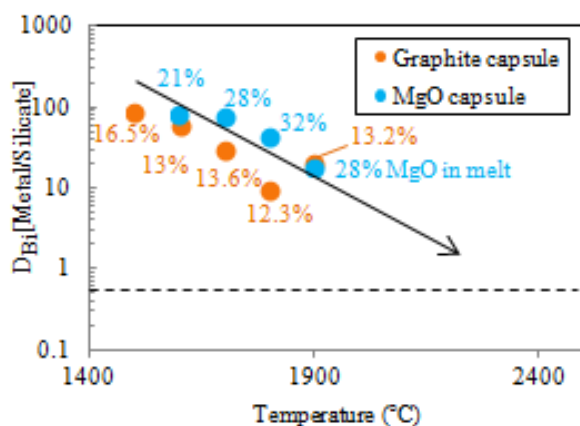


Fig.2. Partition coefficients with respect to temperature for Bi. Data show a decreasing trend with increasing temperature. The dashed line is the D_{Bi} required for core-mantle equilibrium in the Earth.

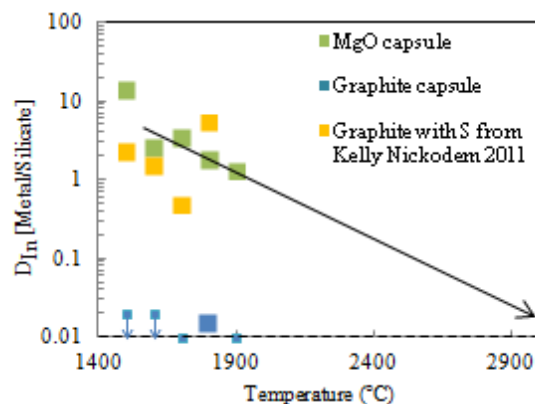


Fig.3. Partition coefficients with respect to temperature for In. Data show a decreasing trend with increasing temperature. The dashed line is the D_{In} required for core-mantle equilibrium in the Earth.

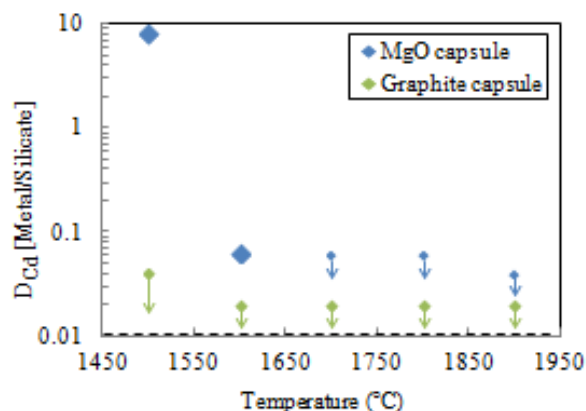


Fig.4. Partition coefficients with respect to temperature for Cd. The dashed line is the D_{Cd} required for core-mantle equilibrium in the Earth.

References: [1] Righter, K. et al. (2011) *Earth Planet Sci. Lett.*, 304, 158-167. [2] Albarede, F. (2009) *Nature*, 461, 1227-1233. [3] Lewis, R.D. et al. (1993) *Meteorites*, 28, 622-628. [4] Li and Agee CB. (1996) *Nature*, 381:686-689. [5] Righter K, Drake MJ. (1997) *Earth Planet Sci. Lett.*, 146:541-53.